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(54) POLYESTER PACKAGING MATERIAL

(57)Abstract:

PURPOSE: To improve resistance to gas-permeability and the interlayer separability of a multilayer structure in a polyester resin packaging material.

CONSTITUTION: A polyester packaging material is of a multilayer structure made up of a polyethylene terephthalate component and a polyethylene isophthalate component copolymerized with an aliphatic hydroxy carboxylic acid of at most 8 carbon atoms in an amount of 5-60wt.%. The packaging material is excellent in mechanical strength and transparency.

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* NOTICES *

1. This document has been translated by computer using translation software, PAT-Transer V7 produced by Cross Language Inc. So the translation may not reflect the original precisely.
 2. The word which can not be translated is expressed by Japanese character.
 3. The drawings and tables are not translated.
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[Claims for the Patent]

[claim 1]

A superior polyester wrapping material of the gas permeability which formed the polyethylene iso phthalate ingredient which 5-60 mol % inter-polymerization made aliphatic oxycarbonic acid of less than or equal to polyethylene terephthalate ingredient and carbon number 8 in a multilayer construction resistance.

[claim 2]

A wrapping material as claimed in claim 1 that there is the inter-polymerization polyethylene iso phthalate ingredient in quantity of 3-25 mol % of all polyester for an aliphatic oxycarbonic acid unit.

[claim 3]

A wrapping material as claimed in claim 2 that there is the inter-polymerization polyethylene iso phthalate ingredient in quantity of 5-20 mol % of all polyester for an aliphatic oxycarbonic acid unit.

[claim 4]

A wrapping material as claimed in claim 1 that the aliphatic oxycarbonic acid is chosen as by glycolic acid, hydracrylic acid, four - hydroxybutyric acid, five - Oki ti valeric acid, six - Oki ti caproic acid, seven - Oki Shie naan Japanese spaniel acid, eight - Oki ti caprylic acid and those functional derivative.

[claim 5]

A wrapping material as claimed in claim 4 that the aliphatic oxycarbonic acid is glycolic acid.

[claim 6]

A wrapping material as claimed in claim 1 that an inter-polymerization ratio of the aliphatic oxycarbonic acid is 10-50 mol %.

[claim 7]

A wrapping material as claimed in claim 1 that inherent viscosity of the polyethylene terephthalate ingredient is 0.5-1.5.

[claim 8]

A wrapping material as claimed in claim 1 that inherent viscosity of the polyethylene iso phthalate ingredient is 0.3-1.5.

[Detailed Description of the Invention]

[0001]

[Industrial Application Field]

The present invention relates to a polyester wrapping material having a superior multilayer construction of physical property such as hardness of machine without the delamination which it be superior to gas permeability resistance about a polyester wrapping material in detail, and win, transparency.

[0002]

[Prior Art]

Polyethylene terephthalate is used from the superior mechanical property, chemical property widely by fiber, a film, an industrial resin, but is used as field of application such as a bottle, a cup, a tray more recently. Such a field of application requires gas permeability resistance from a point of a contents save, but if polyethylene terephthalate is compared with polyolefin resin as shown in polyethylene, if although high gas permeability resistance is had, it is compared with glass, aluminum, it cannot be said to have always enough gas permeability resistance.

[0003]

Thus a method to improve in gas permeability resistance of polyethylene terephthalate is examined, much proposal is made. By way of example only, gas permeability material such as polyvinylidene chloride, polyethylene - vinyl acetate Ken apparition, polyethylene iso phthalate resistance is coated onto polyester or methods (56 Japanese Patent Laid-Open No. - 151648 bulletin) a method (57 Japanese Patent Laid-Open No. - 10640 bulletin, a European patent laid open 105826 bulletin and 59 Japanese Patent Laid-Open No. - 196316 bulletin) to blend gas permeability material resistance, amount of preferred orientation of a polyester molded article are given to a method (54 Japanese Patent Laid-Open No. - 117565 bulletin, 56 Japanese Patent Laid-Open No. - 64839 bulletin, 59 Japanese Patent Laid-Open No. - 39547 bulletin, a European patent laid open 105825 bulletin), polyester to laminate, and to be able to improve gas permeability resistance are suggested. However, there is a limit for improvement of gas permeability resistance by a method to raise amount of preferred orientation, there is a problem in salvage recycling after use by a method to use gas permeability material resistance as again.

[0004]

Adhesive property with polyester is bad, and a delamination is waked up to use the resin which was different from polyester in a method polyvinylidene chloride in particular and polyethylene - vinyl acetate Ken apparition are coated, to laminate together and, as a result, transparency of vessel is lost, and there is not and is disadvantageous from point of salvage.

[0005]

In addition, because, in a method polyethylene iso phthalate is coated, to laminate, both strata are the same polyesters, there is not such a shortcoming, but even if it is laminated for hardness as resin based on polyethylene iso phthalate oneself, it is fragile, and bend in

polyethylene terephthalate to make have hardness as vessel, when independent, it is about the same, it is fleshy, and it is necessary to do, it gets heavy as the whole vessel, and a good point of synthetic resin vessel including light-weight will be lost. Gas permeability resistance is not enough, too.

[0006]

In addition, it is difficult in conditions of molding of polyethylene terephthalate by a method (the 4,424,242nd United States Patent specification) to laminate polyglycolic acid to get a molded article having hardness of an enough machine, and gas permeability resistance is insufficient.

[0007]

Furthermore, (the 4,403,090th United States Patent specification) that the polyalkylene isophthalate which inter-polymerization was able to put aliphatic dicarboxylic acid from carbon number 4 to 12 in as polyester for wrapping materials for polyethylene terephthalate is suggested to is not satisfied with this polyester to improve gas barrier characteristics of a polyethylene terephthalate wrapping material.

[0008]

[Objects of the Invention]

The object of the present invention is to provide the polyester wrapping material which it was superior to physical properties such as mechanical strength, transparency, and gas permeability resistance was able to be superior to.

[0009]

[Constitution of the Invention]

The present invention is a superior polyester wrapping material of gas permeability including the polyethylene isophthalate constituent which 5-60 mol % inter-polymerization made aliphatic oxycarbonic acid of less than or equal to polyethylene terephthalate ingredient and carbon number 8 resistance.

[0010]

Terephthalic acid is assumed main acid with "polyethylene terephthalate" in the present invention, it is the polyester which assumes ethylene glycol a main glycol component. As for the polyethylene terephthalate, other acid and a glycol component may be able to leave copolymerization in the range that does not lose the characteristic properties. In addition, 如 such as trimeric acid, pentaerythritol comes, and, in the range where a molecule is linearity substantially, monofunctional compound such as multifunctional compound or benzoic acid may be able to leave copolymerization.

[0011]

This polyethylene terephthalate ingredient does in much the same way as normal polyethylene terephthalate, and it is produced. When it is used as a food packaging material, germanium oxide is preferable in safe hygiene than antimony trioxide for polymerization catalyst, but if polyolefin fits a positive list of a hygiene meeting, it is preferable why.

[0012]

The mechanical strength which is high from physical properties is desirable for inherent viscosity of a polyethylene terephthalate ingredient of the present invention. Preferably less than 1.5 are more than 0.6 more than 0.5 to be concrete.

[0013]

As for "the inter-polymerization polyethylene iso phthalate" which is useful for a wrapping material of the present invention, 95-40 mol % contains an ethylene iso phthalate unit, 5-60 mol % contains an aliphatic oxycarbonic acid unit of less than or equal to carbon number 8. Gas permeability resistance was found by inter-polymerization doing the aliphatic oxycarbonic acid which hung in polyethylene iso phthalate without what was improved conspicuously expecting.

[0014]

When an inter-polymerization ratio is less than 5 mol %, fragility based on isophthalic acid becomes remarkable, and there can be the thing that strength of a provided wrapping material becomes insufficient. On the other hand, hardness of machine falls physical property of thermostability in a plastic treatment and a molded article particularly when an inter-polymerization ratio is beyond 60 mol %, it is unfavorable. Preferably an inter-polymerization ratio of aliphatic oxycarbonic acid is 10-50 mol %.

[0015]

For aliphatic oxycarbonic acid of less than or equal to carbon number 8, glycolic acid, hydracrylic acid (three - Oki ti propionic acid), four - hydroxybutyric acid, five - Oki ti valeric acid, six - Oki ti caproic acid, seven - Oki Shie naan Japanese spaniel acid, eight - Oki ti caprylic acid are given. For example, as for the aliphatic oxycarbonic acid, these functional derivative may be low-grade alkyl ester, the molecule lactone which it is spin-dried, and became ringed (for example, β - プロピオラクトン, γ - butyrolactone, δ - パレロラクトン, ϵ - カプロラクトン). Among these compounds, glycolic acid is the preferable. Preferably preferably higher than 0.45 are particularly desirable for inherent viscosity of inter-polymerization polyethylene iso phthalate more than 0.4 less than 1.5 more than 0.3.

[0016]

Of course, the above-mentioned inter-polymerization polyethylene iso phthalate may include other inter-polymerization constituent in the range that does not lose the characteristic properties. In addition, monofunctional compound such as glycerin, trimethylolpropane, pentaerythritol, trimerit acid, trimesic acid, pyro merit acid, multifunctional compound such as tricarballylate, o - benzoylbenzoic acid, naphthoic acid may be coupled in the field which a polymer can consider to be linearity substantially. Because when preferably a polyfunctional compound can leave inter-polymerization with quantity of 0.1-0.5 mol % in particular, creep properties of a provided molded article is improved, preferred.

[0017]

Inter-polymerization polyethylene iso phthalate can be produced by a method similar to

polyethylene terephthalate. By way of example only, transesterification is performed isophthalic acid, aliphatic system oxycarbonic acid and an ethylene glycol are used, and esterification reaction is performed or and lower alkyl ester (for example, dimethylester) of isophthalic acid, functional derivative (for example, low-grade alkyl ester, lactone) of aliphatic system oxycarbonic acid and ethylene glycol are used, because polycondensation succeeds in getting provided reaction product more, it can be produced. In addition, it is performed same as above methods except that addition of aliphatic system oxycarbonic acid or the functional derivative is changed before a polycondensation reaction start, and it can be produced. On that occasion it is preferable to use an esterification catalyst, an ester interchange catalytic substance, a polycondensation catalytic substance, heat stabilizer. These catalytic substances, stabilizer can use polyester, a thing known as a catalytic substance of polyethylene iso phthalate, stabilizer in particular. In addition, for example, other additive may use pigmenting drug, fluorescent whitening agent, anti-oxidant, UV absorber, antistat, fire retardant if necessary.

[0018]

It is preferable to use a phosphorus compound for heat stabilizer, and, for this case, it had better be used in quantity of 50-150 millimeters mol % as phosphorus. In addition, it is desirable that anti-oxidant uses in quantity of 0.1-1 % by weight as against weight of inter-polymerization polyethylene iso phthalate.

[0019]

The wrapping material of the present invention formed the above-mentioned polyethylene terephthalate ingredient and inter-polymerization polyethylene iso phthalate ingredient in a multilayer construction. In a polyester wrapping material of the present invention, what there is in the quantity that 3-25 mol %, of all polyester becomes 5-20 mol % for an aliphatic oxycarbonic acid unit in particular is desirable for an inter-polymerization polyethylene iso phthalate ingredient.

[0020]

When a polyester wrapping material of the present invention is formed by a multilayer construction, there is not restriction in particular for the stratum formation, and there is not restriction in number of layer particularly either, but five levels are at most desirable for the fact top and are preferable with a thing having constitution to 3. In addition, generally copolymerization polyethylene iso phthalate constituent should be formed as interlayer when preferred, it does with three levels of configuration to form a polyethylene terephthalate ingredient as the most inner layer of a wrapping material.

[0021]

For example, for a wrapping material of the present invention, a provided container is exemplified by forming processes with drawing such as a bottle, a drinking cup. In addition, it may be the vessel which it is bottomed, and vessel, the pipe which deep draw forming does an abrasive sheet of non-drawing, and is provided are done, and was drawn. Furthermore, a

vacuum or a thing of air-pressure forming form of held tray includes abrasive sheet or it. For example, for a method to get these wrapping materials, there is well-known 押出吹込成形方法 or two 軸延伸吹込成形方法 in the case of a bottle conventionally, but two 軸延伸吹込成形方法 is profitable. After, in the case of two 軸延伸吹込成形方法, inflatable geometry thing namely container outrider compact was heated at draft temperature, pipe precursor compact or it makes draw by recording of drawing rod and compressed gas to axially move in 吹込金型内 or to axially move is heated to draft temperature, it is bottomed, and it is done after drawing in differential of feed velocity and taking care of velocity, it makes a hoop direction draw by having a thing recorded of compressed gas, and incorporation can be done in form of a bottle.

[0022]

For example, container outrider compact having a multilayer construction uses by what is molded from an inner layer by normal injection molding machine or making machine having several fusion injection unit step by step sequentially or making machine having an injection cylinder of plural number block, it is bottomed, and is got one end of the multilayer pipe which formed polyethylene terephthalate melted in locking pressure movement in single die once and copolymerization polyethylene iso phthalate by by formation succeeding in getting the copolymerization polyethylene iso phthalate which timing is moved, and inner, injected of continuation and in alteration or polyethylene terephthalate injected by what is injected approximately at the same time earlier in right side out layer later in interlayer or multilayer extruder by what is done.

[0023]

Container outrider compact or application of heat of multilayered pipe outrider compact can be usually performed in heat ovens having normal exothermic body such as a block heater or an infrared heater next. Draft temperature in case of multilayered container outrider compact is the approximately same as draft temperature of container outrider compact comprising polyethylene terephthalate simple substances.

[0024]

[Effects of the Invention]

Be superior to gas permeability resistance and a polyester wrapping material of the present invention can be superior to physical property such as hardness of a machine, transparency. In addition, a polyester wrapping material of the present invention having a multilayer construction has superior characteristic that there is not a delamination more.

[0025]

[Examples]

The present invention is explained below by means of an example concretely. Each property value of an example measured by the following method.

[0026]

Inherent viscosity of a polymer, $[\eta]$: It was calculated from the solution viscosity which measured o - chlorophenol solution of a polymer at 35 degrees Celsius.

[0027]

Bottle run-away impact shock strength resistance

Weighing is inserted in a bottle oral region in the condition that done sodium bicarbonate 14g are not mixed with citric acid aqueous solution in a bottle directly in water 1,000g and the product made in back polyethylene bag which citric acid 14g were filled with in a bottle, 打栓 was done in product made in aluminium cap promptly. Development succeeded in getting CO₂ by a bottle was waved so that sodium bicarbonate and a citric acid water solution inserted in a 打栓後 bottle joined enough, and mixing, and CO₂ was done with the condition which was filled with in a bottle the aqueous solution which succeeded in getting compression dissolution. A bottle explosion ratio when it made the CO₂ filling bottle was kept 5 degrees Celsius, and bottle basilar part fall to concrete floor line than height of 1.5 meters as downward 24 hours later was examined.

[0028]

Carbon dioxide of a bottle resistance is permeable

A filling bottle is moved to atmosphere of back 20 degrees Celsius that held the CO₂ filling bottle that the compression dissolution succeeded in getting CO₂ 4.0 times Volume by the end of H₂O in the case of run-away strength measuring method resistance similarly of a bottle in predetermined temperature, atmosphere of predetermined humidity for predetermined time, CO₂ Volume content fluid temperature measured CO₂ pressure in a bottle in the condition which was 20 degrees Celsius, and to remain in was measured.

[0029]

But it is CO₂ Volume = V_{CO_2}/V_{H_2O}

It is H₂O fluid volume in a bottle OV_{H_2O}

0 degrees Celsius of the CO₂ which VCO₂ dissolves in H₂O liquid phase in a bottle, atmosphere reduced volume under one atmospheric pressure

[example 1-4, comparative example 1]]

Polyester A: Be in reactor, and 35 parts of dimethylterephthalate, ethylene glycol 22.4 parts, tetrabutyl titanate 0.002 parts are heated at 150-240 degrees Celsius, heat-up, system are pulled in reduced pressure to addition, 250-280 degrees Celsius slowly, and 0.005 parts phosphorous acid, germanium dioxide 0.0,045 parts are reacted in 1mmHg for 60 minutes at a point in time when 11.5 parts methanol distillation was done [a polymer of η]0.65 was got.], Solid phase polymerization out of nitrogen gas stream is done at 210 degrees Celsius in this more [polyethylene terephthalate of η]0.75 was got.], This is assumed polyester A.

[0030]

Polyester B: Be in reactor, and 17.5 parts dimethyl isophthalate, glycolic acid 6.86 parts, ethylene glycol 11.2 parts, tetrabutyl titanate 0.002 parts are heated to 150-220 degrees Celsius, removal does methanol and aqua, heat-up, system are pulled in reduced pressure to addition, 240-260 degrees Celsius slowly, and 0.005 parts phosphorous acid, germanium dioxide 0.0,045 parts are reacted in 1mmHg for 90 minutes [a polymer of η]0.74 was got.],

This is assumed polyester B.

[0031]

There is two multilayer formation cylinder part, because polyester B adjusts quantity injecting entering, the quantity inside of polyester A at cylinder temperature 200-220 degrees Celsius, cylinder temperature 270-280 degrees Celsius, polyester B (50 degrees Celsius, 24 hours suction drying) are changed into rate as shown in an outside front cover, and, in three levels of injection molding machine that on the other hand enters the other inside, inject polyester A (160 degrees Celsius, five hours hot-air drying) at mold temperature 10 degrees Celsius, trunk 25-26mm outside diameter, radial thickness 3.5mm, one end of full length 155mm were bottomed, and polyester A got a done cylindricality pre-form in three levels of configuration that inner, outer layer, polyester B became interlayer.

[0032]

吹込成形 does the pre-form at pre-form heating temperature 100-130 degrees Celsius in 二軸延伸吹込成形機, trunk 82mm outside diameter, overall height 280mm, trunk radial thickness 320-380 μ m, a bottle of internal space 1040-1050ml were got.

[0033]

Thus, run-away impact shock strength resistance and carbonic acid gas penetrativity of a provided polyester multiple zone bottle resistance are shown to an outside front cover.

[0034]

For comparative purposes, a multilayered bottle comprising polyester A chisels is molded, physical properties of this bottle is matched, and it shows.

[0035]

Though quantity of oxyacid out of a bottle increases with example three or four, the reason why quantity of survival CO₂ decreases is that there is bottle macrosis by creep.

[0036]

[table 1]

[0037]

[example five or six]

In example 3, a glycolic acid ratio in polyester B is changed like example five or six during table 1, at the same time, example 3 and bottle physical property when a biaxial stretching multilayer bottle was made similarly are shown to an outside front cover except that rate 30 of polyester B was done with % by weight among bottles.

[0038]

[example seven or more 9]]

In example 3, first polymer B (example 8) which 0.2 % by weight added (four polymer B (example 7) that was changed of to 100mmol %) as against all acid extends, more, 3,5 pentaerythrityl tetrakis [3 - (- di - t - butyl - - hydroxyphenyl) propionate) in for polymer B in 0.0,148 parts quantity of phosphorous acid to add after ester interchange by production of polyester B and anti-adjustment, 0.069 parts anhydrous bird merit acid (the other which used

polymer B (example 9) that added 0.2 mol %) as against all acid made a biaxial orientation multilayer bottle with example 3 similarly each.) This bottle physical properties is shown for table 1.

[0039]

Because thermostability of polymer B increased in that case of example seven or eight, bottle impact shock strength rises, it was found that creep characteristics were improved in the event of example 9, and survival CO₂ quantity increased.

[0040]

[example 10-15, comparative example two or three]

The other which a predetermined ratio used various oxyacid to show to for table 2 in substitution for glycolic acid as made a biaxial stretching bottle with production of polyester B with example 1 in example 1 similarly.

[0041]

Bottle ability is shown for table 2.

[0042]

[table 2]